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US Army Corps
of Engineers

AN EVALUATION OF SOLIDIFICATION/ STABILIZATION TECHNOLOGY FOR BUFFALO RIVER SEDIMENT
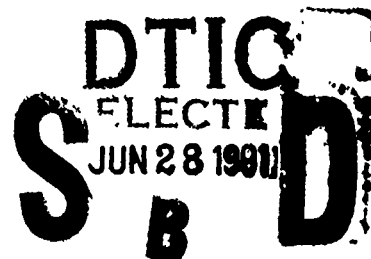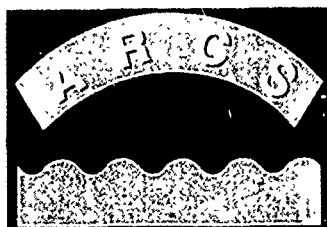
by

Elizabeth C. Fleming, Daniel E. Averett
Michael G. Channell, Bret D. Perry

Environmental Laboratory

DEPARTMENT OF THE ARMY
Waterways Experiment Station, Corps of Engineers
3909 Halls Ferry Road, Vicksburg, Mississippi   39180-6199

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Elizabeth C. Fleming, Daniel E. Averett,
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13. ABSTRACT (Maximum 200 words)

The Buffalo River drains a 446-square-mile (1,155-sq-km) watershed in western New York State and discharges into Lake Erie at the city of Buffalo. The Buffalo River has been classified by the State of New York as a "fishing and fish survival" stream, but municipal and industrial discharges have degraded the water quality and resulted in a fish advisory for the river. Under the Assessment and Remediation of Contaminated Sediment Program, the US Environmental Protection Agency asked the US Army Corps of Engineers to evaluate solidification/stabilization (S/S) for potential treatment of the contaminated sediments in the Buffalo River.

An evaluation of S/S technology was conducted on the bench-scale level on Buffalo River sediment to determine whether physical and chemical properties of the sediment would be improved. Based on analyses of the untreated sediment,

(Continued)

14. SUBJECT TERMS

Freeze/thaw	Stabilization	Wet/dry
Sediments	TCLP	
Solidification	UCS	

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13. ABSTRACT (Continued).

five metals were selected for evaluation: chromium, copper, lead, nickel, and zinc.

Initial screening tests (ISTs) were conducted on the sediment to narrow the range of binder-to-soil ratios (BSRs) to be prepared in the detailed evaluation. Three binder materials were evaluated: cement, kiln dust, and lime/fly ash. Based on the results of the IST, BSRs were selected for the detailed evaluation. Specimens were prepared by mixing sediment and binder materials in a Hobart K455S mixer and molding the mixture. The specimens were cured for 28 days at 23° C and 98-percent relative humidity.

Physical tests including unconfined compressive strength (UCS), freeze/thaw durability, and wet/dry durability were run to determine if the physical handling properties of the sediment were improved. UCS values less than 50 psi (350 kPa) and loss of 30 percent of the solids from the wet/dry or freeze/thaw specimens constitute failure of the UCS, wet/dry, and freeze/thaw, respectively.

Contaminant release tests were conducted to determine the effectiveness of the binder materials on immobilization of the contaminants. Based on the results of the UCS tests, specimens were selected for evaluation of contaminant release properties. The S/S specimens were subjected to the US Army Engineer Waterways Experiment Station serial leach test (SLT) and the toxicity characteristic leaching procedure (TCLP). The SLT results were compared to the drinking water standards, and the TCLP results were compared to the levels required for the maximum concentration of the contaminant in the TCLP extracts.

PREFACE

This report was prepared for the US Environmental Protection Agency Great Lakes National Program Office (GLNPO) by the US Army Engineer Waterways Experiment Station (WES). This report presents the results of solidification/ stabilization (S/S) studies for contaminated sediment collected from the Buffalo River, near Buffalo, NY.

Under the Assessment and Remediation of Contaminated Sediments (ARCS) Program, a development of the Clean Water Act Amendments of 1987, GLNPO tasked the US Army Corps of Engineers with evaluating treatment technologies for immobilization of contaminants in sediment from the Buffalo River. The US Army Engineer (USAE) Division, North Central, coordinated support to the ARCS Program and GLNPO. The USAE District, Buffalo, collected the sediment samples for evaluation of S/S treatment technologies. WES was responsible for bench-scale evaluation of sediment S/S. GLNPO provided funding and adminis- trative guidance in work performance. Assisting GLNPO in technical review of the results of the study was the ARCS Engineering/Technology Work Group, a group of engineers and scientists with responsibility for monitoring work performed under the ARCS Program.

The bench-scale treatability evaluation was performed by Ms. Elizabe ı C. Fleming and Messrs. Daniel E. Averett, Michael G. Channell, and Bret D. Perry of the Water Supply and Waste Treatment Group (WSWTG), Environmental Engineering Division (EED), Environmental Laboratory (EL), WES. Technical review of the report was performed by Dr. M. John Cullinane and Mr. Tommy E. Myers, EED. Analyses of leachates generated as the result of leaching tests were performed by the Analytical Laboratory Group, EL, under the direction of Ms. Ann B. Strong. Unconfined compressive strength tests were performed by the Materials and Concrete Analysis Group, Concrete Technology Division, Structures Laboratory, WES.

The work was conducted under the direct supervision of Mr. Norman R. Francingues, Chief, WSWTG, and under the general supervision of Dr. Raymond L. Montgomery, Chief, EED, and Dr. John Harrison, Chief, EL. Ms. Jessica S. Ruff of the Information Technology Laboratory edited the report.

COL Larry B. Fulton, EN, was Commander and Director of WES. Dr. Robert W. Whalin was Technical Director.

This report should be cited as follows:

CONTENTS

CONVERSION FACTORS, NON-SI TO SI (METRIC)
UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

Multiply	By	To Obtain
degrees (angle)	0.01745329	radians
feet	0.3048	meters
gallons (US liquid)	3.785412	cubic decimeters
inches	2.54	centimeters
miles	1.609347	square kilometers
pounds (force) per square inch	6.894757	kilopascals
square inches	6.4516	square centimeters
square miles	2.589998	square kilometers

AN EVALUATION OF SOLIDIFICATION/STABILIZATION TECHNOLOGY
FOR BUFFALO RIVER SEDIMENT

PART I: INTRODUCTION

Background

1. The Buffalo River drains a 446-square mile* watershed in western
New York State and discharges into Lake Erie at Buffalo, NY. The Buffalo
River Area of Concern is illustrated in Figure 1. Although the State of
New York has classified the Buffalo River as a "fishing" stream, municipal and
industrial discharges into the river have degraded water quality. As a
result, taking of fish for consumption from the river has been restricted by
the State of New York. Although abatement efforts have reduced the discharges
of contaminants to the river, residual contaminants in bottom sediments are
believed to contribute to continued water quality impairment of the river
(New York State Department of Environmental Conservation (NYDEC) 1989).

Solidification/Stabilization

2. Effects of contaminated sediment on water quality can be reduced by
a number of control or treatment technologies. Alternatives for reducing or
eliminating contaminant transport from the sediment into the water column
include isolating the contaminated sediment from the water by capping with a
layer of clean sediment or chemically solidifying the sediment in place.
Other remediation options involve removing the contaminated material from the
waterway and treating or disposing of the dredged material so that contami-
nants are removed, destroyed, immobilized, or efficiently contained within a
disposal site. However, treatment options that efficiently extract or destroy
contaminants are expensive, and unrestricted disposal in a confined disposal
facility provides the potential for leaching of contaminants and pollution of
groundwater or surface water.

3. Solidification/stabilization (S/S) is a promising treatment
technology for containing and immobilizing dredged material contaminants

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* A table of factors for converting non-SI units of measurement to SI
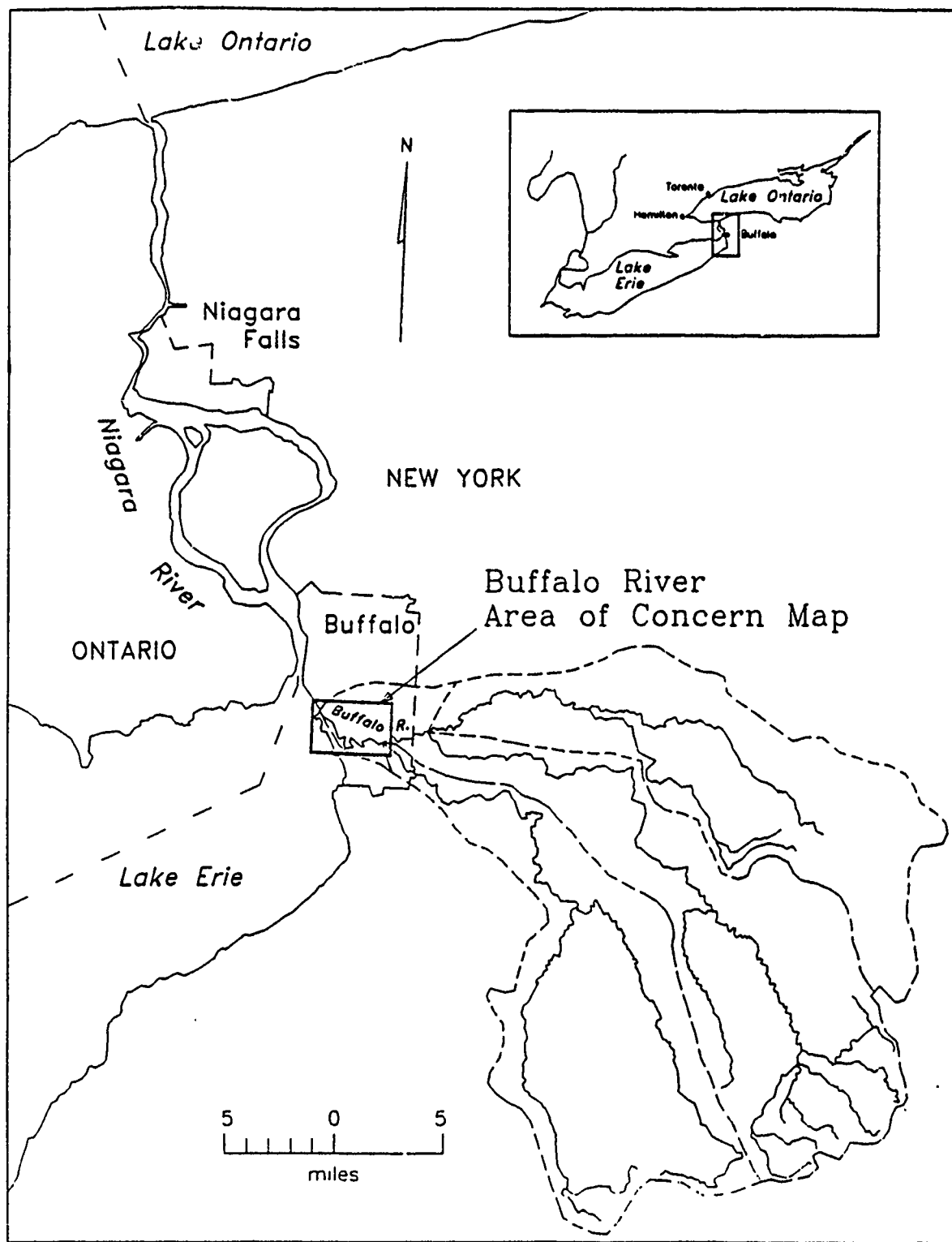   (metric) units is presented on page 4.

Figure 1. Buffalo River Area of Concern (from NYDEC 1989)

within a disposal site. S/S technology has been applied in Japan to bottom sediments containing toxic substances (Otsuki and Shima 1982, Kita and Kubo 1983) and in the United States to industrial wastes (Cullinane, Jones, and Malone 1986; US Environmental Protection Agency (USEPA) 1989). Laboratory investigations of S/S of dredged material have been performed for Indiana Harbor, Indiana (Environmental Laboratory 1987); Everett Bay, Washington (Palermo et al. 1989); and New Bedford Harbor, Massachusetts (Myers and Zappi 1989). While S/S is not a solution to every disposal problem, the technology offers improved physical characteristics that reduce the accessibility of water to contaminated solids and reduced leachability for many contaminants.

4. Myers and Zappi (1989) have described S/S for dredged material. Solidification is the process of eliminating the free water in a semisolid by hydration with a setting agent(s) or binder(s). Stabilization can be both physical and chemical. Solidification usually provides physical stabilization but not necessarily chemical stabilization.

5. Physical stabilization refers to improved engineering properties such as bearing capacity, trafficability, and permeability. Alteration of the physical character of the material to form a solid material reduces the accessibility of water to the contaminants within a cemented matrix and entraps or microencapsulates the contaminated solids within a dimensionally stable matrix. Since most of the contaminants in dredged material are tightly bound to the particulate fraction, physical stabilization is an important contaminant immobilization mechanism (Myers and Zappi 1989).

6. Chemical stabilization is the alteration of the chemical form of the contaminants to make them resistant to aqueous leaching. S/S processes are formulated to minimize the solubility of metals by controlling pH and alkalinity. Anions, which are more difficult to bind in insoluble compounds, may be immobilized by entrapment or microencapsulation. Chemical stabilization of organic compounds may be possible, but the mechanisms involved are poorly understood (Myers and Zappi 1989).

7. Binders include cements, pozzolans, or thermoplastics (Cullinane, Jones, and Malone 1986). In certain instances, proprietary additives may also be added to the process. Results of reactions of binders to the contaminated sediment are not always predictable due to varying contaminant types and concentrations within the test material. Therefore, laboratory leach tests must be conducted on a sediment-specific basis. Discussions of S/S processes are

provided in Malone and Jones (1979); Malone, Jones, and Larson (1980); and USEPA (1986a).

8. Binders selected for potential application to Buffalo River sediment are:

   a. Portland cement.

   b. Lime/fly ash.

   c. Kiln dust.

These binders were selected because of their nonproprietary nature and ready availability. They have been used in a number of S/S studies at the US Army Engineer Waterways Experiment Station (WES), including assessment of best demonstrated available technology for a number of listed hazardous wastes. Portland cement addition results in the formation of a concrete-like monolith. Lime/fly ash pozzolanic processes combine the properties of lime and fly ash to produce low-strength cementation. Kiln dust processes involve the addition of kiln dust to eliminate free liquids and usually form a low-strength solid.

9. Because the above binder systems are not always effective for organics, addition of activated carbon to the portland cement process was investigated as a fourth S/S process. The purpose of the activated carbon is to adsorb contaminants. The activated carbon particles along with the adsorbed contaminants may then become physically bound within the solid matrix produced by the cement.

Objective and Scope

10. The objectives of this study were to:

    a. Evaluate the effects of S/S treatment on contaminant mobility for Buffalo River sediment.

    b. Evaluate improvements in the physical handling properties of Buffalo River sediment by S/S.

    c. Determine if activated carbon addition to a portland cement process will enhance contaminant immobilization.

11. The scope of the study involved laboratory preparation of S/S samples using Buffalo River sediment and the following binders/additives: portland cement, lime (slaked)/fly ash, kiln dust, and portland cement with powdered activated carbon. A range of weight binder-to-weight wet sediment ratios (BSRs) were screened, and an optimum ratio was selected for detailed evaluation for each binder process. Effectiveness was measured by comparing

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leaching results, unconfined compressive strength (UCS), and durability under wet/dry and freeze/thaw cycles.

Organization of the Report

12. This report is divided into four parts:

   a. Part I provides the background information around which this study evolved.

   b. Part II describes the materials and methods used to evaluate S/S of the Buffalo River sediment and S/S with carbon-treated sediment.

   c. Part III discusses the results of the physical and chemical tests run on the S/S sediment and S/S carbon-treated sediment.

   d. Part IV presents conclusions and recommendations regarding S/S of Buffalo River sediment.

PART II: S/S MATERIALS AND METHODS

Approach

13. This study was conducted in five phases:

   a. Phase I: Sample collection. Sample collection was performed by the US Army Engineer District, Buffalo. Samples were composited and shipped to WES by the USEPA Research Laboratory, Duluth, MN.

   b. Phase II: Screening tests. Initial screening tests were performed to narrow the range of binder dosages for preparing the test specimens. Moisture contents were evaluated to determine whether addition of water was necessary and to evaluate the success of homogenization efforts.

   c. Phase III: Preparation of test specimens for detailed evaluation. The sediment was mixed with binders and cured under controlled conditions.

   d. Phase IV: Physical and Chemical Testing. Based on results of the UCS testing, specimens were selected for detailed evaluation of contaminant leachability and wet/dry and freeze/thaw testing.

   e. Phase V: Report Preparation. Results from the physical and chemical tests were used to develop conclusions and recommendations regarding S/S of Buffalo River sediment.

Sediment Sample Collection and Analysis

14. The sediment was collected by the Buffalo District using a clamshell dredge from the approximate location shown in Figure 2. The samples were placed in 5-gal plastic buckets and shipped to the USEPA laboratory in Duluth, MN for thorough homogenization and splitting. Samples were shipped from Duluth to the WES in seven 5-gal plastic buckets. Upon receipt at the WES, the samples were placed in a cooler at 4° C until tested.

15. Each of the seven 5-gal buckets was thoroughly mixed for 10 min in a Hobart H600T mixer. Triplicate samples were collected from each bucket and analyzed for moisture content as an assessment of the similarity among buckets. Results of these tests are presented in Table 1. Comparison of the results of the moisture contents conducted on each container indicates
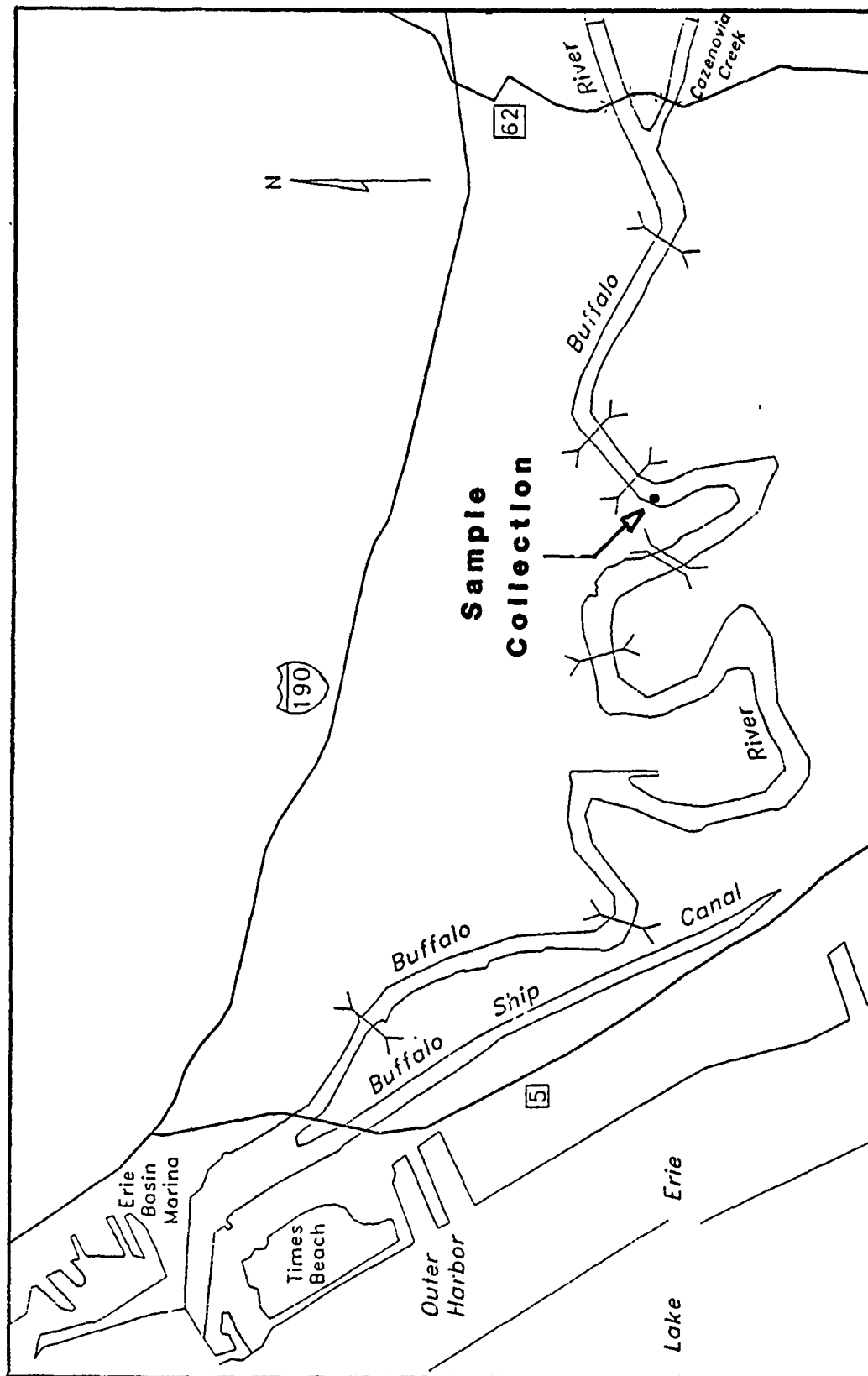
Figure 2. Location sample collection for Buffalo River sediment (after NYDEC 1989)

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Table 1

Solids Concentration* for Buffalo River Sediment

| Replicate | Container Number | | | | | | |
	1	2	3	4	5	6	7
A	57.5	57.7	57.8	57.8	57.9	57.9	57.9
B	57.5	57.8	57.7	57.8	57.9	58.0	58.0
C	57.7	57.6	57.9	57.9	57.8	57.9	58.0
Average	57.6	57.7	57.8	57.8	57.9	57.9	58.0

Composite average 57.8

* Expressed as percent dry solids by weight per total weight of sediment.

that the buckets were similar in moisture content. Average moisture content varied by less than 0.4 percent for the seven buckets. Based on these results, homogenization of the total sample was determined to be adequate, and no further intermixing of buckets was performed. Replicate samples of solidified sample were prepared from three buckets labeled A, B, and C. Water addition was not necessary for Buffalo River sediment, although this is sometimes required in the S/S process for improved mixing. A composite sample from one bucket was collected for use in conducting a chemical screen for contaminants. Results of this screening-level analysis are presented in Table 2. Based upon this characterization, metals to be analyzed in the leaching tests were selected. Metals selected for analysis were chromium, copper, lead, nickel, and zinc. This same sample was subsequently subjected to more detailed analysis for contaminants selected for the evaluation of S/S.

Preparation of Test Specimens

Preparation of initial
screening test specimens

16. The purpose of the initial screening test is to narrow the range of BSRs necessary to solidify/stabilize the sediment test specimens. A wide range of BSRs was used for the initial screening test. Table 3 represents the matrix of specimens prepared in the initial screening test. After mixing the binder materials with the sediment, the initial screening test specimens were cured at 23° C and 98 percent relative humidity in an environmental chamber for 48 hr.

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Table 2
Screening-Level Characterization of Buffalo River Sediment

Parameter	Concentration μg/g (dry weight)
Base neutral acids	7.17
Cyanides	1.29
Oil and grease	9,100
Phenol	<4.7
Total PAHs	5.91*
Total PCBs	<0.01
Total chlorinated pesticides	0.0017
Total organic carbon	21,400
Total volatile organic compounds	1.47
Aluminum	9,900
Arsenic	5.7
Barium	76.0
Cadmium	1.44
Chromium	56.6
Copper	59.0
Iron	27,700
Lead	81.0
Manganese	541
Mercury	0.606
Nickel	34.0
Silver	0.200
Zinc	151

* PAH compounds reported in Appendix A, Table A1.

Table 3

Matrix of Specimens Prepared for Initial Sediment/Binder Screening for the Buffalo River Sediment

Binder-to-Sediment Ratio	Number of Specimens
Cement-Sediment	
0.1	1
0.3	1
0.5	1
0.7	1
0.9	1
1.1	1
1.4	1
	Total: 7
Kiln Dust-Sediment	
0.1	1
0.3	1
0.5	1
0.7	1
0.9	1
1.1	1
1.4	1
	Total: 7
Lime/Fly Ash-Sediment	
0.1/0.1	1
0.1/0.3	1
0.1/0.5	1
0.3/0.1	1
0.3/0.3	1
0.3/0.5	1
0.5/0.1	1
0.5/0.3	1
0.5/0.5	1
	Total: 9

17. After the 48-hr curing period, the specimens were removed from the environmental chamber, and the cone index (CI) test was performed (Headquarters, Department of the Army 1971). The CI value is reported as force per unit surface area (pounds per square inch (psi)) required to push the cone through the test material surface at a rate of 72 in./min. Depending upon the projected strength of the specimen and calibrations of the cone penetrometer, one of two cone penetrometers (each with 30-deg right circular cones) was selected. The WES penetrometer with a surface area of 0.5 sq in. was selected for specimens with a CI less than 100 psi. An airfield penetrometer with a surface area of 0.2 sq in. was selected for specimens with a CI greater than 100 psi. The maximum measurement on the airfield penetrometer is 750 psi. Therefore, measurements of the CI value that were greater than 750 psi were reported as >750 psi.

18. From the information provided by the initial screening tests, BSRs for the preparation of test specimens for detailed evaluation were selected. A minimum BSR and appropriate range of formulations was selected for each binder based on the CI value and experience with other sediments and soils. The specimens prepared in the initial screening test were not evaluated further.

Preparation of test
specimens for detailed evaluation

19. Three BSRs were selected for cement and kiln dust, and nine BSRs were selected for lime/fly ash. Four carbon-to-sediment ratios (CSRs) were prepared with one cement BSR after the results of the UCS tests for cement, kiln dust, and lime/fly ash had been obtained. Cement with carbon was chosen based on higher UCS values reported for cement than for the other binders. The matrix of test specimens prepared for detailed evaluation is presented in Table 4.

20. Sediment and binder were mixed in a Hobart K455S mixer for 5 min. The container was scraped so that particles adhering to the sides of the container were mixed. After scraping, the sediment and binder were mixed for an additional 5 min. Replicate batches were prepared from separate 5-gal buckets of sediment. Specimens were identified as originating from bucket A, B, or C.

21. After mixing, the sediment/binder mixture was poured into 2- by 2- by 2-in. brass molds for UCS and Toxicity Characteristic Leaching Procedure (TCLP) analysis. A light coating of grease was added to the molds prepared

Table 4

Matrix of Specimens Prepared for Detailed Evaluation

Binder	Binder-to-Soil Ratios
Cement	0.2, 0.4, 0.6
Kiln dust	0.2, 0.4, 0.6
Lime/fly ash	0.2/0.2, 0.2/0.4, 0.2/0.6 0.4/0.2, 0.4/0.4, 0.4/0.6 0.6/0.2, 0.6/0.4, 0.6/0.6
Cement/carbon	0.2/0.01 0.2/0.001 0.2/0.0001 0.2/0.00001

for UCS testing to aid in removal of the specimens from the molds and to eliminate damage to the cubes as they were extruded from the molds. Serial Leach Test (SLT) samples were poured into plastic molds with a diameter of 4-3/4 in. and a height of 3-1/2 in. The wet/dry and freeze/thaw sediment/binder specimens were poured into plastic, cylindrical molds with a height of 2-1/4 in. and a diameter of 1-5/8 in. Immediately after the specimens were poured into the molds, they were vibrated on a Sentron model VP61D1 vibration table to reduce air-filled voids. At the higher BSRs, vibration was not an effective method for reduction of air-filled voids. As a result, the specimens were tamped according to ASTM C 109-88 with a Model CT-25A tamper (American Society for Testing and Materials 1988a).

22. The molded specimens were cured in an environmental chamber at 23° C and 98 percent relative humidity for a minimum of 24 hr. The specimens were removed from the molds when they had developed sufficient strength to be free standing. After they were removed from the molds, the specimens were returned to the environmental chambers to cure for 7 to 28 days at a constant temperature of 23° C and 98 percent relative humidity.

Addition of powdered activated carbon

23. Based upon the UCS results of the cement-treated sediment, specimens were prepared with cement and powdered activated carbon as a fourth S/S process. Cement was selected because of its considerably higher physical strength compared with kiln dust and lime/fly ash. A wide range of CSRs was

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evaluated with a BSR of 0.2 cement. The samples were prepared according to the same procedures previously discussed.

Physical and Contaminant Release Testing

Unconfined compressive strength

24. The UCS was determined according to ASTM method C 109-88 (ASTM 1988a). Tamping and vibration were the only modifications of this method. The UCS was evaluated after 7, 14, and 21 days of cure on one of the triplicate mixtures. The UCS was evaluated in triplicate after 28 days of cure and reported as an average in pounds (force) per square inch. The force required to fracture the specimen was determined with a Tinius Olsen Super L compression apparatus. The surface area of the cube was determined with a Fowler Max-cal caliper.

Contaminant Release Testing

25. _Toxicity Characteristics Leaching Procedure._ The TCLP was conducted in accordance with the USEPA protocol described in 40 CFR Part 268, Appendix I (_Federal Register,_ 7 November 1986). Triplicate tests were performed for each binder and for the untreated sediment, and a blank was included with each binder tested. Prior to the leaching test, the S/S samples were crushed with a mortar and pestle and passed through a 0.375-in. standard sieve. Leaching fluid was selected based upon the pHs of a mixture of sample and distilled water or a mixture of sample, distilled water, and 1.0 $\underline{N}$ hydrochloric acid (HCl). If either pH was <5.0, the leaching fluid consisted of 5.7 ml acetic acid (HOAC) per liter extraction fluid and 64.3 ml 1.0 $\underline{N}$ sodium hydroxide (NaOH) per liter extraction fluid (extraction fluid 1). If both pHs were >5.0, the extraction fluid consisted of 5.7 ml HOAC per liter extraction fluid (extraction fluid 2). After mixing the sample with leaching fluid for 18 hr, leachate samples were filtered through a Whatman GF/F glass fiber filter.

26. _Serial Leach Test._ Contaminant desorption characteristics for the untreated and treated sediment were evaluated using the SLT described in Myers and Zappi (1989). This test uses successive challenges of the solid material with distilled/deionized water at a 1 part dry solids to 4 parts water ratio by weight. Each step in the process includes tumbling the solid-water mixture for 24 hr, followed by separation of the solids from the leachate by centrifugation and filtration. The succeeding step uses the solids recovered

from the preceding separation. Seven steps were performed for the untreated sediment, and five steps were performed for the treated specimens. Anaerobic conditions were maintained using a nitrogen blanket for leaching the untreated sediment. Treated specimens were crushed and sieved by the same method used for the TCLP. Liquid-solid separation for the leachates was accomplished by centrifugation and filtration. The SLT was performed in triplicate, and a blank was included for each specimen tested.

27. All BSRs were subjected to the TCLP. The initial tier of analyses included analytical testing of the lowest BSR that met a minimum UCS criterion of 50 psi. Only one BSR sample from each binder process was evaluated for the SLT. The criterion for a 50-psi minimum was chosen based on information found in the Office of Solid Waste and Emergency Response Policy Directive 9487.00-2A (USEPA 1986b). This was used for selection of the BSRs for TCLP chemical analysis and SLT. All samples not analyzed were archived in a cooler at 4° C. All CSR samples were subjected to the TCLP. The highest and lowest CSR samples were submitted for analytical testing, and the remaining carbon samples were archived in a cooler at 4° C.

Wet/dry and freeze/thaw testing

28. For wet/dry and freeze/thaw testing, the same BSR samples evaluated for the first tier of contaminant release tests were subjected to wet/dry and freeze/thaw testing in order to provide the opportunity for comparison between contaminant release test results and durability of the S/S products. Wet/dry and freeze/thaw durability tests were conducted on samples with the highest CSR in order to determine the effect of carbon on the durability of the S/S carbon-treated samples.

29. The wet/dry test was performed according to ASTM D 4843-88 (ASTM 1988b) after a 28-day cure time. Specimens were run through 12 cycles of the test, and the weights of the samples were measured after each cycle to determine the amount of sample lost in the cycle. The test was performed on each binder in triplicate with a control for each replicate.

30. The freeze/thaw test is a weathering test that consists of freezing the samples and subsequently thawing them to constitute a cycle. The method is similar to the wet/dry test and is nearing adoption by an ASTM subcommittee. Twelve freeze/thaw cycles were evaluated on triplicate samples and controls. Specimens are alternately frozen for 24 hr, followed by covering with water to allow thawing at room temperature for 24 hr. At the conclusion of the thaw cycle, the specimens are removed from the water and returned to the

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freezer. The water is evaporated to determine the dry weight of the specimen lost during the cycle. Loss of more than 30 percent of the original sample weights constitutes failure of the test. Controls are stored in an environmental chamber at 23° C and 98 percent relative humidity during the freeze cycle.

PART III: DISCUSSION OF RESULTS

Physical Strength Testing

Initial screening test results

31. The results for the initial screening tests on all binders are
presented in Table 5. Samples for seven BSRs each for cement and kiln dust
and for nine BSRs for lime/fly ash were prepared. No ISTs using carbon were
prepared because low carbon dosages were not expected to affect the IST
results for the cement binder.

32. Cement binder. The cement samples demonstrated low strength at a
BSR of 0.1, indicating that specimens for detailed evaluation should be pre-
pared at BSRs greater than 0.1. At a BSR of 0.3, the cement binder gained
significant strength, >750 psi. As a result, specimens were prepared for
detailed evaluation at BSRs of 0.2, 0.4, and 0.6.

33. Kiln dust binder. Kiln dust samples had very low strength develop-
ment at a BSR of 0.1. At BSRs of 0.5 and 0.7, the kiln dust gained signifi-
cant strength. These results indicated that increasing the BSR above 0.1
would provide the required UCS values for the detailed evaluation. BSRs of
0.2, 0.4, and 0.6 were selected as a suitable range for detailed evaluation.

34. Lime/fly ash binder. The lime/fly ash binder samples had very low
strength at 0.1 lime/0.1 fly ash, indicating that higher ratios should be
selected for detailed evaluation. Increasing the addition of lime or fly ash
increased the cone index value significantly. Increasing both the lime and
fly ash additions from 0.1/0.1 to 0.3/0.3 caused an increase from approxi-
mately 11 to 265 psi, respectively. Nine lime/fly ash combinations were
selected, beginning at a minimum BSR of 0.2 lime and 0.2 fly ash.

UCS results

35. Raw data for UCS measurements are presented in Table A2. The
development of physical strength of the solidified specimens as measured by
UCS at 7, 14, 21, and 28 days of curing is illustrated in Figures 3 and 4.
These graphs show that all binders met the minimum 50-psi criterion after the
first 7 days of curing, except for the 0.6 lime/0.4 fly ash and 0.6 lime/0.6
fly ash. The low strengths for these formulations are probably due to insuf-
ficient moistu e to accommodate the hydration of lime. These mixtures
appeared drier during mixing than for BSRs involving lower lime ratios. For

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Table 5

Matrix of Initial Screening Test Results

for the Buffalo River Sediment Samples

| Binder-to-Sediment Ratio	48-hr Cone Index Value, psi - Replicate Readings		
Cement-Sediment			
0.1	140	160	160
0.3	750+	750+	750+
0.5	750+	750+	750+
0.7	750+	750+	750+
0.9	750+	750+	750+
1.1	750+	750+	750+
1.4	750+	750+	750+
Kiln Dust-Sediment			
0.1	15	10	15
0.3	85	80	77
0.5	370	450	420
0.7	690	750+	750+
0.9	750+	750+	750+
1.1	750+	750+	750+
1.4	750+	750+	750+
Lime/Fly Ash-Sediment			
0.1/0.1	10	12	10
0.1/0.3	55	50	50
0.1/0.5	600	650	500
0.3/0.1	100	90	95
0.3/0.3	250	280	270
0.3/0.5	700	750	750
0.5/0.1	650	610	450
0.5/0.3	750	700	750
0.5/0.5	750+	750+	750+

21
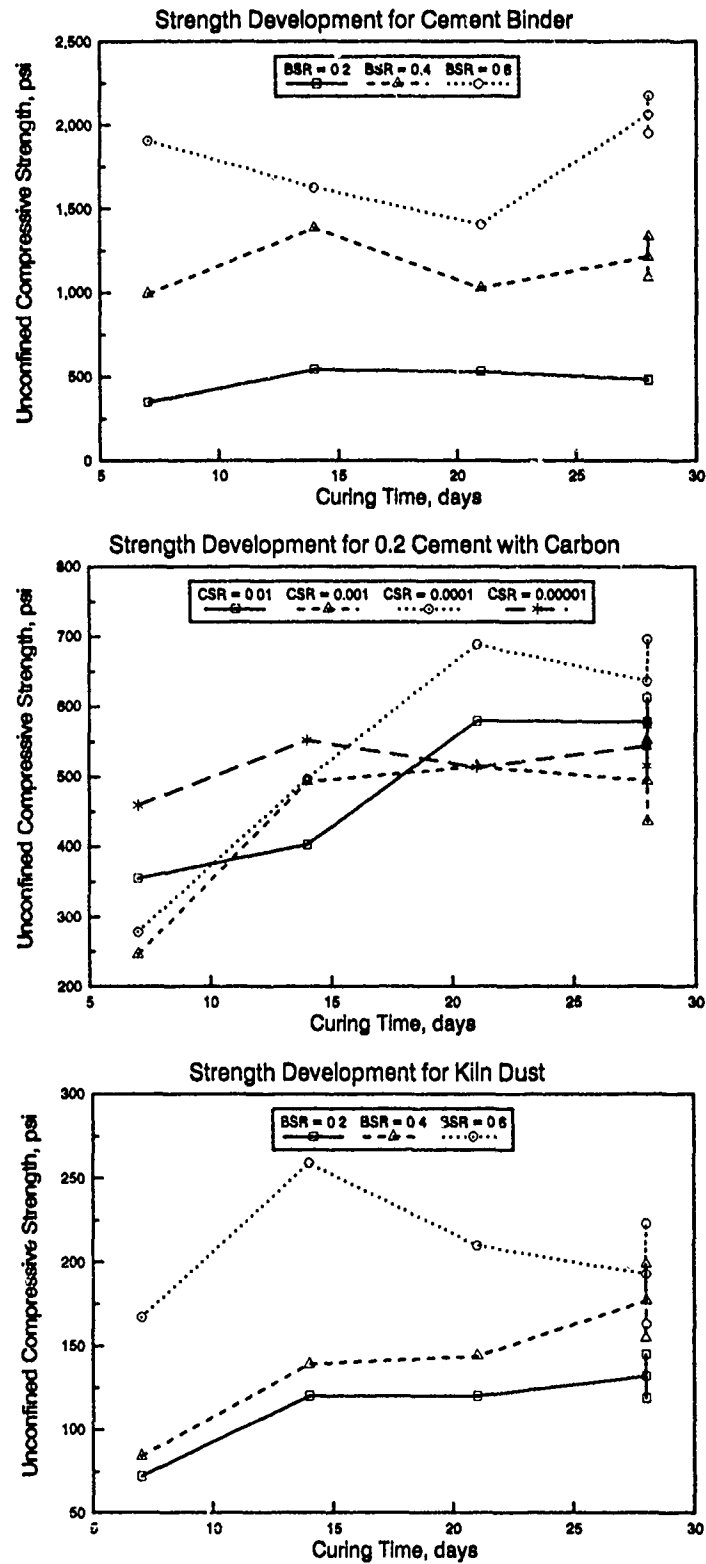
Figure 3.   Strength development for cement,
cement/carbon, and kiln dust (bars at
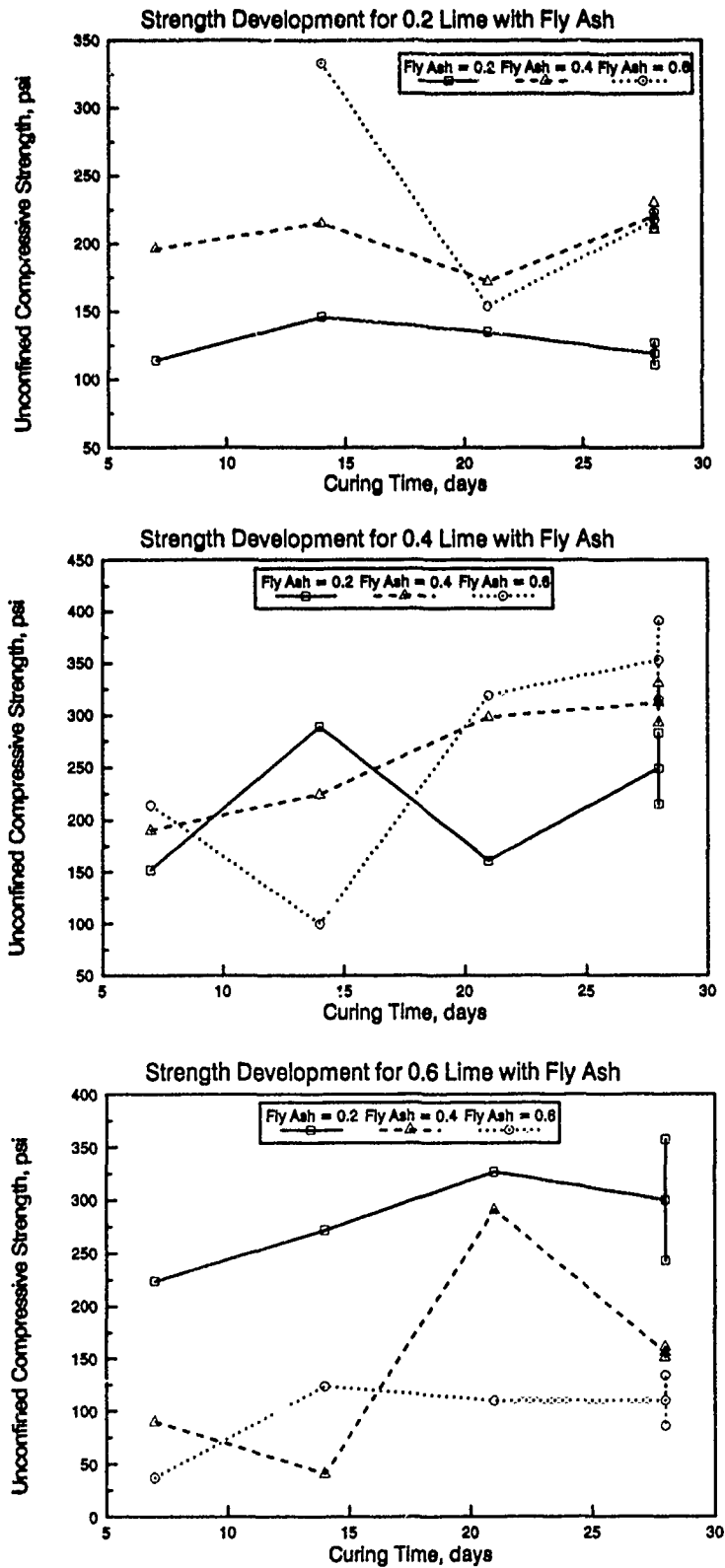   28 days indicate standard error)

Figure 4. Strength development for lime/
fly ash binder (bars at 28 days indicate
standard error)

other lime ratios and for cement and kiln dust, increased BSRs generally increased the UCS (see Figure 5).

36. The UCS should generally increase with increased curing time. Several of the curves shown in Figures 3 and 4 show an apparent decrease in strength with time. Possible explanations for these uncharacteristic curves are dehydration of the specimen or interference with the solidification process by contaminants in the sediment. Experimental differences may also contribute to the problem. Triplicate analyses were performed only for the 28-day specimens. The coefficients of variation for these replicates, which were measured at the same time, ranged from 0.79 to 38 percent with a median value of 14 percent. Therefore, small differences in UCS values measured at different times are probably not significant.

37. Comparison among binders for the 28-day UCS is shown in Figure 5. The 28-day UCS values were all greater than 100 psi. The cement binder produced considerably greater strength than kiln dust or lime/fly ash. The lowest cement ratio produced a UCS greater than any of the ratios evaluated for kiln dust and lime fly ash. The maximum UCS for the formulations prepared for this study was 2,063 psi for the 0.6 cement BSR. Addition of carbon to the cement produced slight variations in UCS but no apparent trend in UCS with respect to carbon concentration. Increasing the lime content from 0.2 to 0.4 increased UCS, but the highest lime ratio coupled with 0.4 and 0.6 fly ash ratios demonstrated a decrease in strength.

Wet/Dry and Freeze/Thaw Testing

38. Results of the wet/dry and freeze/thaw tests are presented in Tables 6 and 7, respectively. One BSR was evaluated for each binder, and one CSR for cement was evaluated. The specimens were subjected to 12 cycles of the test, and a weight of the sample was taken after each cycle to determine the amount of sample lost. A total loss of more than 30 percent of the sample weight during the 12 cycles constitutes failure (ASTM 1988b). The test was run on each binder in triplicate with a control for each replicate.

Wet/dry tests

39. Cement binder. There was no significant loss of material from the specimens during the 12 wet/dry cycles. The average material lost was less than 0.5 percent of the original weight (Table 6). The control specimens lost
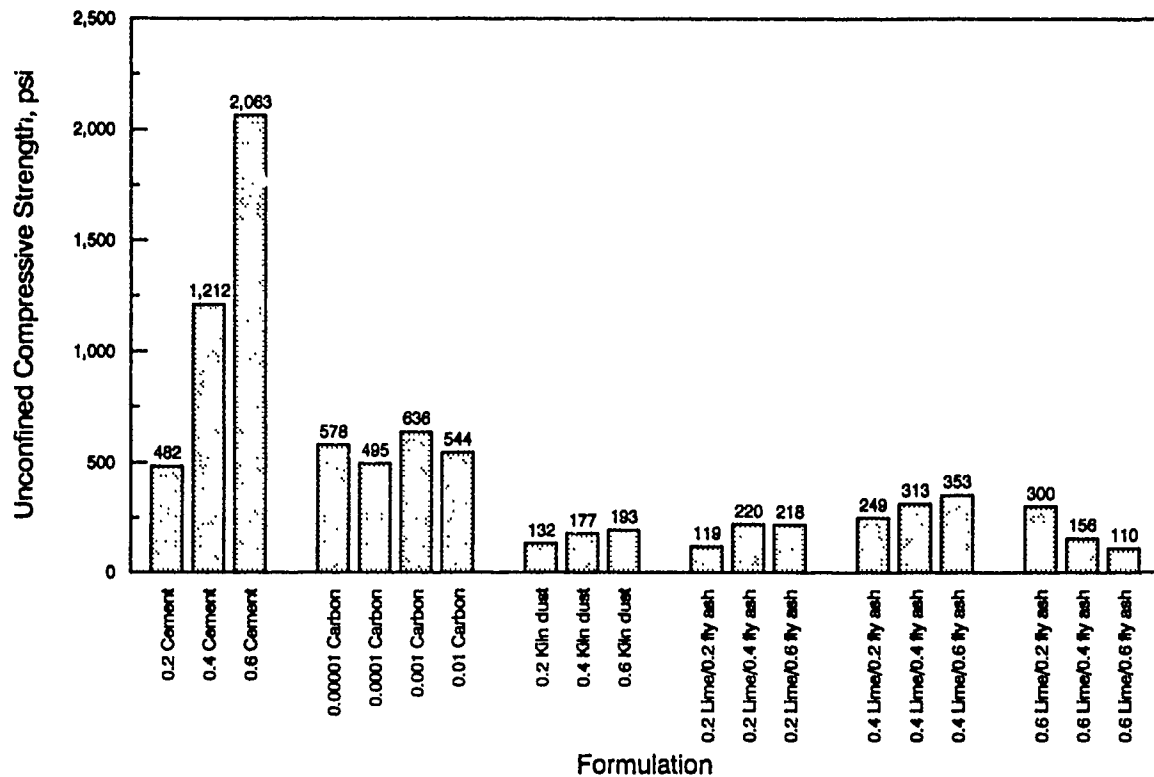
Figure 5. 28-day unconfined compressive strength for
solidified/stabilized sediment

an average of 0.4 percent of the total weight. Although the test specimens lost slightly more sample than the control specimens, the 0.2 BSR for cement passed the test.

40. Carbon treatment with cement binder. The BSR for cement was 0.2, and the CSR was 0.01. Like the cement specimens, the cement/carbon specimens lost little of their original weight during the 12 wet/dry cycles. The average weight loss of the test specimens was 0.6 percent. The control specimens lost an average of 0.3 percent of the total weight of the sample. The cement/carbon mixture passed the wet/dry test. Based upon results of the wet/dry and freeze/thaw tests, no change in durability was associated with the addition of carbon to the portland cement process.

41. Kiln dust binder. The BSR for kiln dust was 0.2. The average weight lost after the test was 1.4 percent of the original sample weight. The control specimens lost an average of 1.8 percent of the original weight also. The 0.2 kiln dust BSR passed the wet/dry test.

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Table 6
Results of Wet/Dry Tests on Buffalo River Sediment

Process	Percent Lost (Replicate No.)		
	1	2	3
Cement (0.2 BSR)			
Specimen	0.415	0.545	0.385
Control	0.349	0.550	0.232
Cement/carbon (0.2/0.01 BSR/CSR)			
Specimen	0.541	0.441	0.678
Control	0.296	0.272	0.345
Kiln dust (0.2 BSR)			
Specimen	0.430	1.59	2.06
Control	1.74	2.06	1.51
Lime/fly ash (0.2/0.2 BSR)			
Specimen	0.251	4.11	3.76
Control	4.47	0.000	0.502

Table 7
Results of Freeze/Thaw Tests on Buffalo River Sediment

Process	Percent Lost (Replicate No.)		
	1	2	3
Cement (0.2 BSR)			
Specimen	3.90	0.898	1.91
Control	0.284	0.392	0.411
Cement/carbon (0.2/0.01 BSR/CSR)			
Specimen	0.496	0.000	6.59
Control	0.246	0.221	0.239
Kiln dust (0.2 BSR)			
Specimen	100	100	100
Control	0.415	0.388	0.419
Lime/fly ash (0.2/0.2 BSR)			
Specimen	100	100	100
Control	0.213	0.219	0.191

42. *Lime/fly ash binder.* The lime/fly ash BSR for wet/dry testing was
0.2 lime/0.2 fly ash. The average weight lost for the test specimens after
the test was completed was 0.3, 4.1, and 3.8 percent for the three replicates.
All specimens passed the wet/dry test. The average weight lost after the test
for the control specimens also varied, but the average was 1.7 percent.
Although there were variances within the lime/fly ash wet/dry test, all speci-
mens passed the 30-percent weight loss criterion.

Freeze/thaw tests

43. *Cement binder.* The average total weight lost for the triplicate
specimens for 0.2 cement was 2.2 percent of the total weight. The highest
amount of material lost in one cycle was 0.8 percent of the total weight. The
control specimens lost an average of 0.35 percent of the total weight of the
sample. A total loss of more than 30 percent of the sample during the
12 cycles constitutes failure. All cement specimens and controls passed the
freeze/thaw test.

44. *Carbon treatment with cement binder.* The test specimens lost an
average of 2.4 percent of the total weight of the specimen during the test.
The control specimens lost an average of 0.2 percent of the total weight of
the specimen. All the cement/carbon specimens and controls passed the
freeze/thaw test.

45. *Kiln dust binder.* All of the test specimens lost 100 percent of
the total weight of the sample during the second cycle of the test. When
water was added to the specimens they crumbled into fragments, none of which
was 70 percent of the total weight. The control specimens lost an average of
0.4 percent of the total weight of the sample. The 0.2 kiln dust ratio failed
the test. The kiln dust test specimens were not further tested after failure.

46. *Lime/fly ash binder.* All of the test specimens lost 100 percent of
the total weight of the specimen during the second cycle of the test. When
water was added to the specimens they crumbled into fragments, none of which
was 70 percent of the total weight. The control specimens lost an average of
0.2 percent of the total weight of the specimen. The lime/fly ash test speci-
mens were not further tested after failure.

TCLP

47. Laboratory data for TCLP testing of sediment and solidified/
stabilized sediment are provided in Appendix A, Tables A3 and A4. Heavy metal
concentrations in the leachate produced by the TCLP are illustrated in Fig-
ure 6. This figure compares average concentrations for TCLP testing of the
sediment to testing of the S/S products. Chromium and copper concentrations
for the untreated sediment were lower by a factor of 4 to 5 than the most
effective of the S/S products. Most of the S/S processes significantly
reduced the leachate concentrations for lead, nickel, and zinc compared to
those for sediment. Cement, cement/carbon, and kiln dust were effective for
lead, nickel, and zinc. However, lime/fly ash was effective only for nickel
and zinc.

Figure 6. Metal concentrations in TCLP leachate
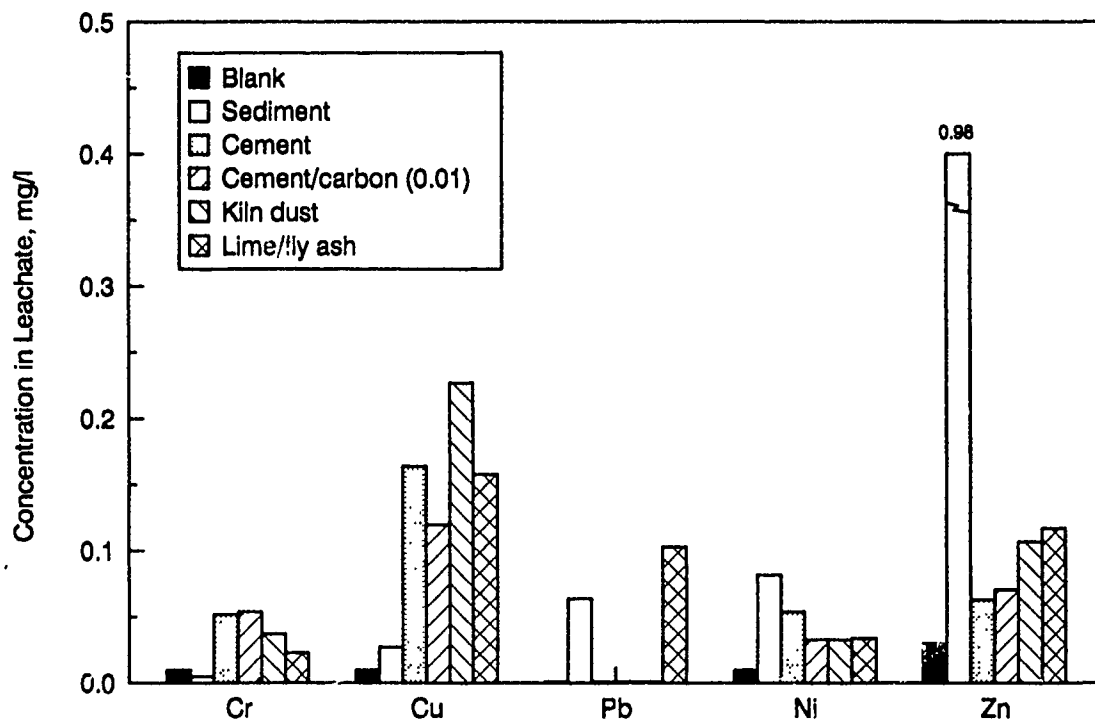
48. None of the TCLP concentrations exceeded regulatory criteria as
defined by the Resource Conservation and Recovery Act (RCRA). Chromium and
lead limits are 5.0 mg/ℓ, but there are no RCRA criteria for copper, nickel,
and zinc. This fact is not surprising considering that the TCLP uses a 20:1
dilution for extracting fluid to solid and that this dilution of the sediment

metal concentrations provided in Table 2 produces levels below the regulatory criteria not only for chromium and lead, but for arsenic, barium, cadmium, mercury, and silver as well. The binders contain some of these metals in concentrations greater than the sediment (see Table A5), but not in high enough concentrations to exceed the regulatory limits. TCLP testing of the binders produced higher chromium concentrations than the Buffalo River untreated and S/S samples (see Table A6).

49. Comparison of leachate concentrations for various treatments does not account for the dilution of the sediment mass being leached by the added mass of the binders. A more valid comparison of immobilization effectiveness can be made by normalizing the leachate data to the dry weight of sediment in the sample being leached. The contaminant mass in the leachate is divided by the contaminant mass contributed by the sediment in the S/S product expressed as dry weight. Effectiveness of the treatment to control leaching can then be expressed as a percent of the contaminant mass in the bulk sediment. Figure 7 represents the results of this normalization procedure for the TCLP results. The impressions and conclusions from this graph are similar to those for the concentration graph (Figure 6) although the percent lost for the S/S samples is slightly greater than results based only on concentration because of the binder contribution to the total weight.

50. Figure 7 shows that S/S processing significantly reduced the amount of nickel and zinc leached from S/S sediment relative to untreated sediment under the leaching conditions of the TCLP for all the S/S processes. The mobility of lead under the leaching conditions of the TCLP was also significantly reduced for cement, cement/carbon, and kiln dust processes. The lime/fly ash process was less effective in immobilizing lead. The differences in metals leachability for S/S sediment versus untreated sediment are probably due to differences in pH during leaching. The final pH for TCLP leaching of untreated sediment was 5.5 (Table A3) while the final pH for S/S sediment ranged from 6.9 to 12.3 (Table A4). Hydroxides of amphoteric metals such as copper, lead, nickel, and zinc have minimum solubilities in the range of pH 9 to 11, depending on the metal (Cullinane, Jones, and Malone 1986). For pH conditions on either side of the solubility minimum, solubility increases. The lower leachate pH for untreated sediment may account for the increased leachability of nickel and zinc in the TCLP test. The alkalinity of the binders buffered the leachate pH for S/S sediment at higher pH values and,
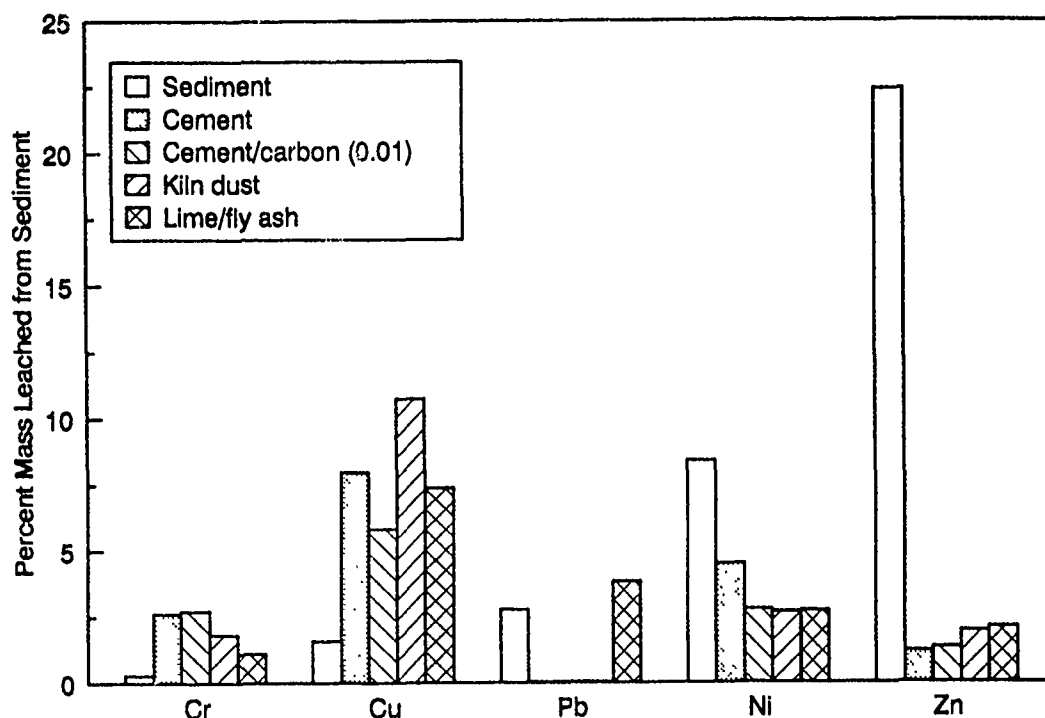
Figure 7. Normalized contaminant mass leached by TCLP

in some cases, in the range of minimum solubilities for nickel and zinc. Figure 7 also shows that S/S processing tended to mobilize chromium and copper under the leaching conditions of the TCLP. The differences may not be significant. In any case, the mobilization of copper cannot be explained by pH differences because, based on pH differences alone, copper should have been immobilized.

SLT

51. Laboratory data for SLT testing of sediment and S/S products are presented in Appendix A, Tables A7-A10. Concentrations of heavy metals in leachate from the SLT are presented in Figures 8-12 for chromium, copper, lead, nickel, and zinc, respectively. These figures compare metal concentrations in leachate produced by SLT testing of sediment to leachates for sediment samples solidified with 0.2 BSR cement, 0.2 BSR kiln dust, and 0.2/0.2 BSR lime/fly ash. Metal concentrations, except for copper, are generally much lower in the SLT compared to the TCLP, probably because the SLT leaching fluid is distilled water rather than acetic acid. SLT leachate concentrations are a better representation of leachate quality for disposal of contaminated dredged material since dredged material would normally be confined separately, not
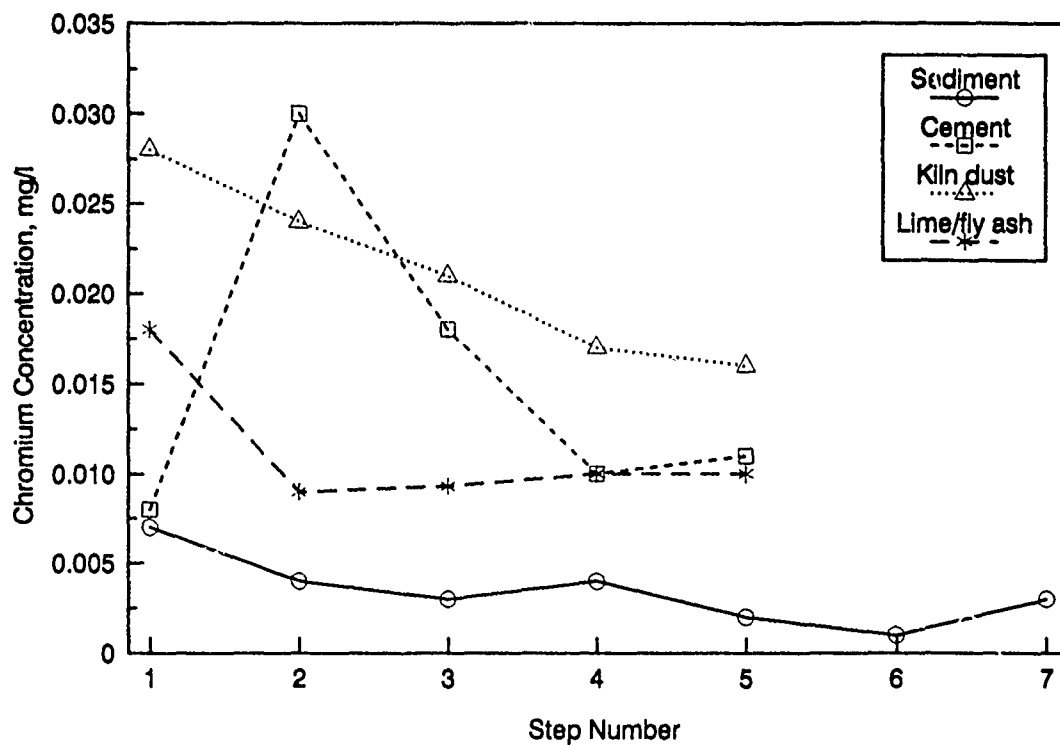
Figure 8.   Chromium concentrations for SLT
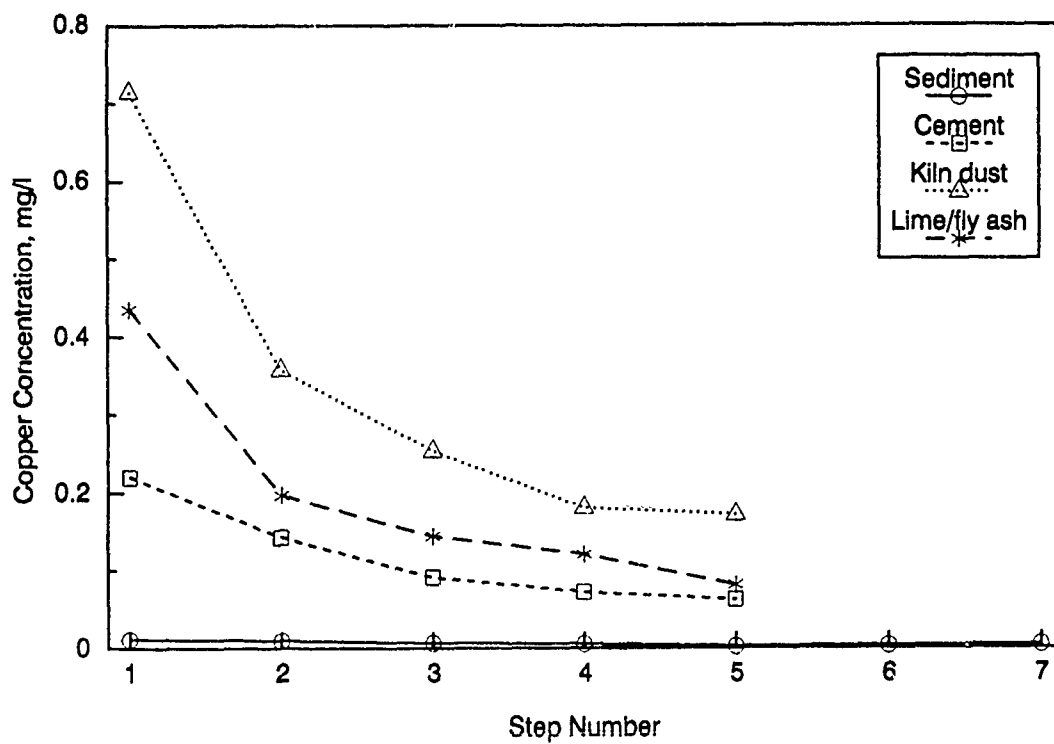
Figure 9.   Copper concentrations for SLT
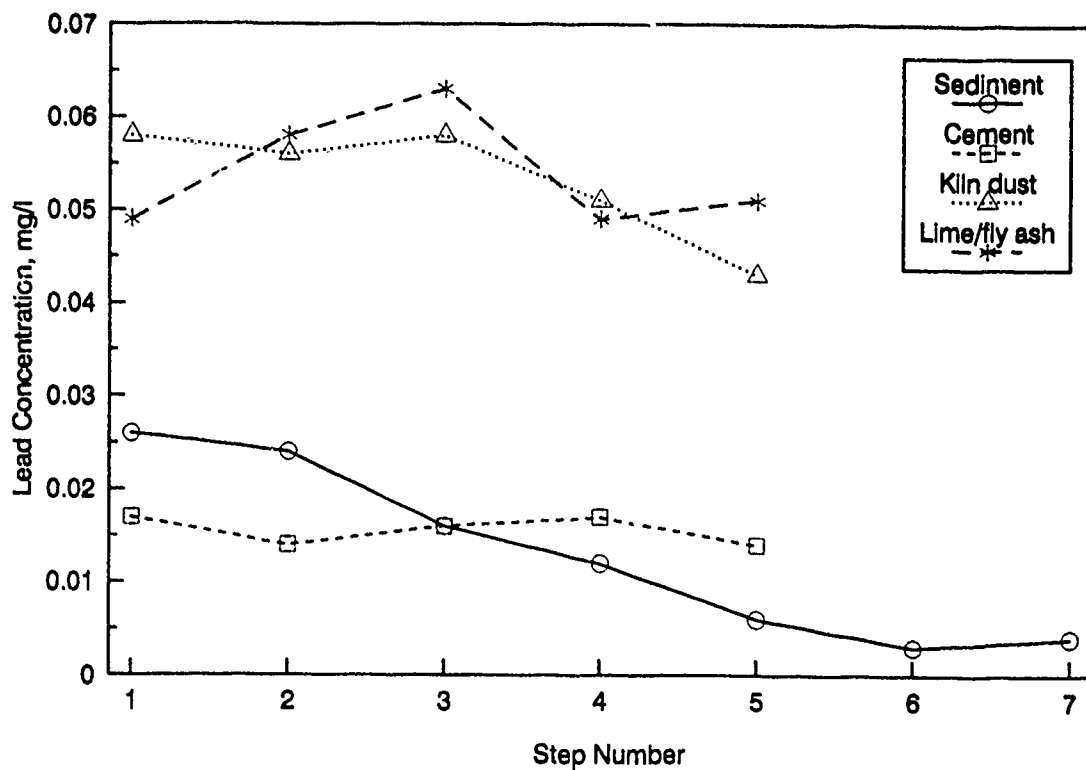
Figure 10. Lead concentrations for SLT
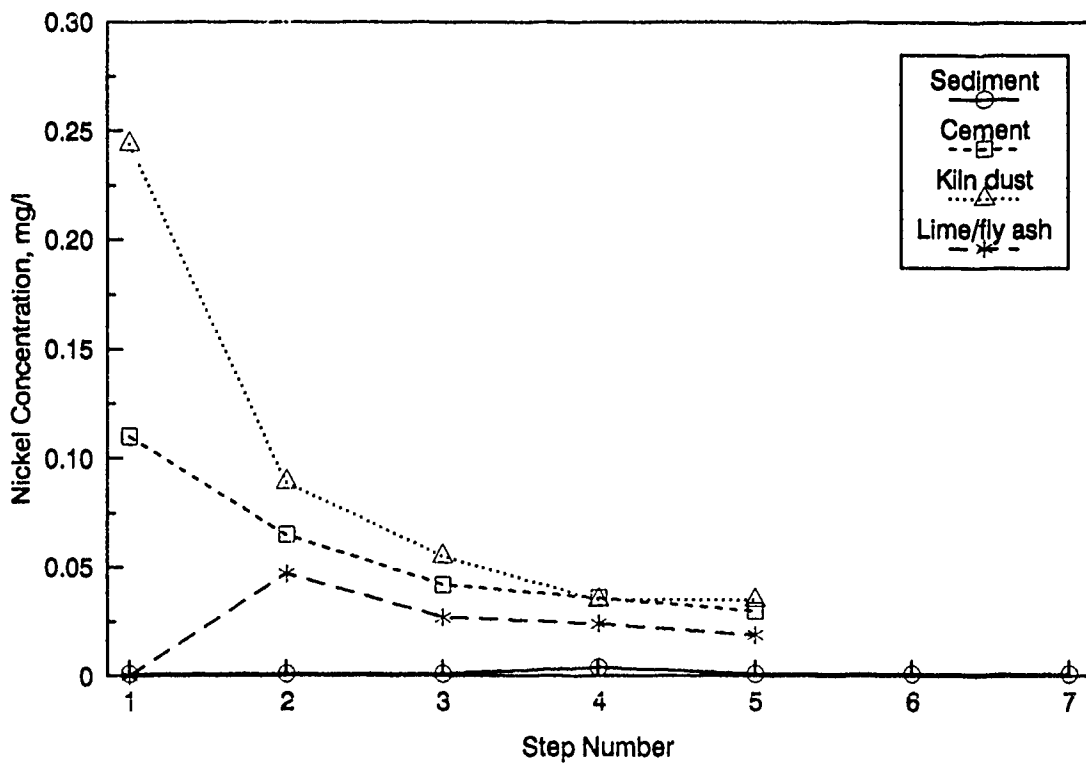
Figure 11. Nickel concentrations for SLT
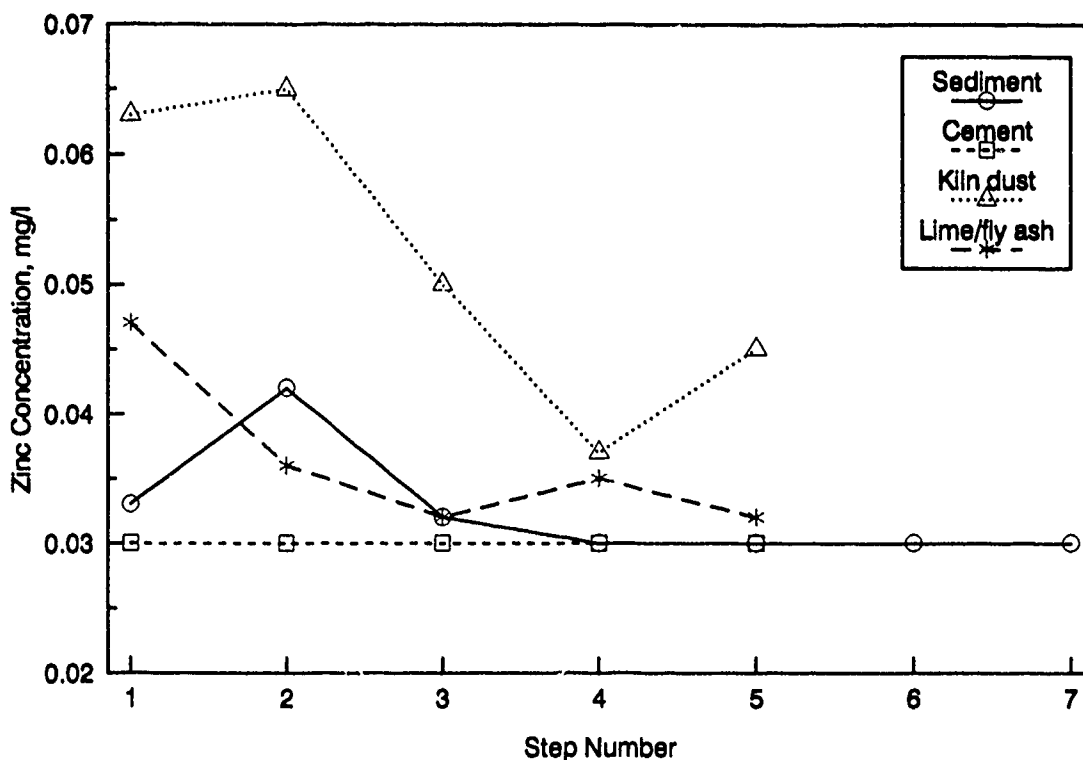
Figure 12. Zinc concentrations for SLT

co-disposed with municipal refuse, which is the case the TCLP was developed to represent. SLT concentrations may be compared directly to maximum contaminant levels for drinking water in order to gauge potential for direct harm to public health by intake. Comparison of SLT concentrations to water quality criteria may also be considered for protection of aquatic life, but leachate concentrations would be significantly diluted by the volume or flow of the waterway.

52. Chromium. SLT results for chromium show that concentrations decrease with step similar to a classical washout curve, i.e., as contaminant mass on the solid phase decreases, contaminant concentration in the leachate also decreases. One exception in Figure 8 is cement during the first two steps. However, analysis of blanks for chromium (Table A8) in this part of the test indicated some contamination, suggesting experimental error. All chromium values were well below the maximum contaminant level for drinking water, 0.05 mg/ℓ and below the water quality criterion recommended by USEPA (1986c) for fresh water, 0.21 mg/ℓ.

53. Copper. SLT results for copper are illustrated in Figure 9. Concentrations for the four treatments evaluated were as follows: sediment

< cement < lime/fly ash < kiln dust. The secondary maximum copper level recommended for public water systems is 1 mg/ℓ (40 CFR Part 143). All leachates were below this maximum. The freshwater chronic water quality criterion for copper is much lower, 0.012 mg/ℓ (USEPA 1986c). Leaching of untreated sediment produced copper concentrations less than this criterion, but all of the S/S samples produced higher concentrations.

54. <u>Lead.</u> Figure 10 illustrates lead concentrations produced by the SLT. Cement-treated sediment produced slightly lower concentrations than untreated sediment, but kiln dust and lime/fly ash concentrations were much higher than the cement-treated and untreated sediment. Lead concentrations for cement-treated and untreated sediment were below the primary drinking water level of 0.05 mg/ℓ; however, all but one of the leachate analyses were above the water quality criterion for lead, 0.0032 mg/ℓ.

55. <u>Nickel.</u> SLT concentrations versus step for nickel are presented in Figure 11. The untreated sediment produced lower leachate concentrations than the S/S sediment samples. However, there are no drinking water standards for nickel, and the water quality criterion is 0.16 mg/ℓ. Only one leachate value, the first step of the kiln dust-treated sediment, was above this criterion. Sediment leachate values were very low, with 0.004 mg/ℓ being the maximum concentration observed.

56. <u>Zinc.</u> Figure 12 illustrates SLT results for zinc. The cement sample produced leachates below the analytical detection limit (<0.03 mg/ℓ) for all five steps of the test. Untreated sediment and lime/fly ash were slightly higher. None of the leachate concentrations was close to the water quality criterion of 0.11 mg/ℓ nor the secondary drinking water level of 5 mg/ℓ.

57. <u>Normalized values.</u> As was discussed for TCLP results, the best way to compare S/S processes is to normalize the data with respect to the sediment contaminant concentration. Figure 13 presents the normalized SLT results expressed as percent of contaminant mass leached from sediment. The mass leached was determined by summing the mass produced by the five steps of the SLT process. For sediment samples, Figure 13 shows the additional mass lost by the seven steps performed for this sample. The maximum percentage leached from the untreated sediment was 0.6 percent. This loss would occur over a period of years. For example, if Buffalo River sediment were placed in a 10-ft lift, had a hydraulic conductivity of 1 × 10^{-5} cm/sec, and remained saturated, one pore volume change would require approximately 1 year. For a solids concentration of 0.58, each step of the SLT represents 5.5 pore
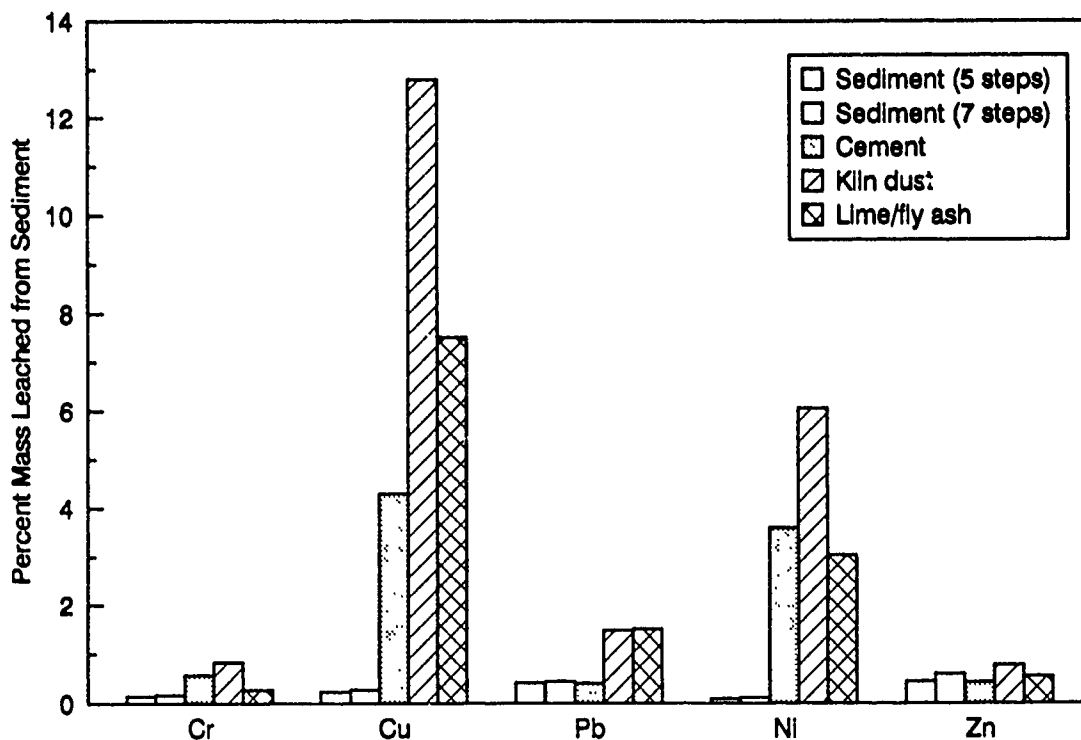
Figure 13. Normalized contaminant mass leached by SLT

volumes, and seven steps represent 38 pore volumes, or 38 years of leachate for the example cited. This analysis assumes that convective transport governs versus diffusive transport (see Myers and Zappi 1989). If water flow through the disposal site were reduced, the time period would be extended. Figure 13 also shows that S/S processes significantly increase the losses of copper and nickel. Nickel is less of a concern because of the higher concentrations tolerated by the environment. Both the SLT and TCLP showed mobilization of copper by S/S processing, indicating that copper mobilization is not a pH effect. Copper losses are the biggest disadvantage of the S/S processes evaluated. Figure 13 also shows that cement was the best overall S/S process evaluated.

Contaminant Release Testing for Organics

58. One objective of this study was to evaluate the effectiveness of S/S processes for polycyclic aromatic hydrocarbons (PAHs). The total PAH concentration in the sediment averaged 5.9 mg/kg. A SLT performed on the untreated sediment produced concentrations in leachate less than 0.01 mg/ℓ for all of the compounds listed in Table A1. PAH analyses of TCLP samples from

untreated and S/S specimens were also less than the detection limit of 0.01 mg/ℓ. The sediment leachate data indicate that PAHs contained in Buffalo River sediment do not leach under the conditions represented by the SLT and TCLP tests. The effectiveness of S/S processes for immobilization of PAHs in Buffalo River sediment cannot be evaluated because of the low PAH concentrations observed by this study.

Alternatives for Application of S/S to Buffalo River Sediment

59. Several alternatives for applying S/S technology to Buffalo River sediment are available. Two basic alternatives based on the method of agent addition and mixing are in situ mixing and plant mixing. The nature of in situ mixing suggests that the solidified material would be confined inside a disposal area, where agent addition, mixing, and curing would take place. Plant mixing offers the opportunity for molding the solidified product into blocks that can be transported elsewhere for disposal, as well as for disposal in a disposal facility.

In situ mixing

60. For addition of the binders to the sediment and in situ mixing, a scow, confined disposal facility or smaller pits would be used. Mechanically or hydraulically dredged material is transported from the waterway to the mixing area. Hydraulically dredged material would likely require a confined disposal facility for temporary storage, and excess water or supernatant would have to be removed. Mechanically dredged material placed in a scow and transported to the disposal site could be mixed with reagent inside the scow and transferred to the disposal area for setting, or the material could be transferred to the disposal area prior to adding and mixing agents. A backhoe, clamshell, or dragline can provide for mixing of the binder and sediment, or a hollow-stemmed auger may be used to inject and mix the binder by a lifting and turning action. The auger injects binder laterally along the perimeter of the facility and, after the material has set, moves upward from the treated material to the next layer of untreated material. Three manufacturers of hollow-stemmed auger systems are Geo-Con, ENRECO, and Envirite. After thorough mixing, the sediment/binder mixture would be allowed to set in a disposal facility or transferred from the scow to a disposal area for setting. The solidified/stabilized material should then be capped with a minimum of 2 ft of

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clean, fine-grained material to protect against freezing/thawing and to reduce infiltration of precipitation.

Mobile plant mixing

61. Mobile plant mixing involves removal of the contaminated sediment from the Buffalo River, mechanical mixing with the binder materials, and depositing the sediment in a prepared disposal site or molding in forms. Typical mixers include ribbon blenders and single- and double-shaft rotary mixers. This application involves site preparation for the unit and preparation of the final disposal area. The advantage of this technique is improved quality control compared to in situ mixing.

Comparisons of Buffalo River Results to Other Sites

62. The WES has performed similar S/S studies on sediments from other waterways, including Indiana Harbor, Indiana, New Bedford Harbor, Massachusetts, and Everett Harbor, Washington. The Indiana Harbor study is most relevant to the ARCS Program because it, like the Buffalo River, is one of the priority areas of concern for the ARCS Program and because it is also a freshwater system.

63. The Indiana Harbor study (Environmental Laboratory 1987) evaluated several different S/S processes, including cement. However, Indiana Harbor results cannot be directly compared to the Buffalo River study because of differences in evaluation procedures, particularly the leachate tests. Indiana Harbor samples were tested using a serial, graded leaching procedure where separate samples of solidified specimen were challenged with distilled water over a range of liquid-to-solid ratios. Tests on the Buffalo River were sequential or step-wise challenges of the same solid sample using fresh distilled water at a 4:1 liquid-to-solids ratio for each of five steps. Liquid-to-solids ratios used for the Indiana Harbor study included a 2:1 and a 10:1, but not 4:1. Leachate concentrations for the first step of the batch leaching tests for the two sites may be roughly compared with the data in Table 8 for the cement process at a 0.2:1 binder-to-solids ratio.

64. These data show that the untreated sediment for the Buffalo River was less contaminated than Indiana Harbor by an order of magnitude. Similar comparisons hold for the batch leaching tests of the two untreated sediments. Samples solidified with portland cement at a 0.2:1 binder-to-solids ratio for both sites demonstrated leachate concentrations that are not very different,

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Table 8

Comparison of Buffalo River S/S Results to Indiana Harbor S/S Results

Sample	Cr	Pb	Zn
Buffalo River			
Sediment, mg/kg	57	81	151
Sediment, Step 1, SLT, 4:1, mg/ℓ	0.007	0.026	0.033
Cement S/S, Step 1, SLT, 4:1, mg/ℓ	0.008	0.017	<0.03
Indiana Harbor			
Sediment, mg/kg	650	879	4,120
Sediment, Step 1, Seq., 4:1, mg/ℓ	0.19	0.37	1.27
Cement S/S, Step 1, Serial, 10:1, mg/ℓ	0.009	0.039	0.033
Cement S/S, Step 1, Serial, 2:1, mg/ℓ	0.007	0.087	0.053

although concentrations for the Buffalo River samples were slightly lower. Solidification/stabilization of Indiana Harbor sediment provides greater environmental benefits than S/S of Buffalo River sediment because of Indiana Harbor sediment's greater potential for contaminant leaching without S/S. UCS values of the cement-solidified samples were 290 psi for Indiana Harbor and 482 psi for Buffalo River.

65. Several other processes, including sodium silicate and Firmix, were evaluated in the Indiana Harbor study. Firmix with a proprietary polymer was the only process that was ranked above the 0.2:1 cement process insofar as immobilization efficiency. Unfortunately, copper was not analyzed for the Indiana Harbor study and cannot be compared to the Buffalo River results. However, increased copper concentrations similar to those observed in this study were observed for a recent solidification study of New Bedford Harbor sediment (Myers and Zappi 1989).

PART IV: CONCLUSIONS AND RECOMMENDATIONS

Conclusions

66.   A bench-scale S/S study was conducted to evaluate the effectiveness of S/S technologies on the physical and chemical properties of Buffalo River sediment.   Physical tests conducted were the UCS, wet/dry, and freeze/thaw. Chemical tests conducted were the TCLP and SLT.   The following conclusions were made as a result of the S/S study on Buffalo River sediment:

a.   Small quantities of binder materials can be added to the sediment to produce UCS values well above the 50-psi criterion.

b.   Water does not have to be added to the S/S process for Buffalo River sediment.

c.   The binders can be easily mixed with the sediment.

d.   The S/S sediment is free standing, with no observed free liquid after 24 hr.   Water associated with the sediment was taken up by the binders, reducing the volume of potential leachate generation.

e.   The cement binder passed all durability tests and provided the highest UCS values.   Kiln dust and lime/fly ash failed the freeze/thaw test.

f.   Based on the TCLP results for crushed specimens, the cement and kiln dust S/S processes were effective in reducing the leachability for lead, nickel, and zinc.   The lime/fly ash process reduced the leachability of nickel and zinc in the TCLP test. Leachability of copper and chromium was increased by S/S processes when compared with untreated sediment for both the TCLP and the SLT.

g.   RCRA regulatory criteria for TCLP results were not exceeded for untreated sediment nor for the S/S products.

h.   SLT results for untreated Buffalo River sediment showed that leachate concentrations were lower than USEPA water quality criteria for copper, chromium, nickel, and zinc.   Lead concentrations were less than one order of magnitude greater than the water quality criterion of 0.0032 mg/ℓ.   Untreated sediment leachates met primary and secondary drinking water standards for the five metals tested.

i.   SLT results for Buffalo River sediment solidified with cement demonstrated that the leachate from this material would meet primary and secondary drinking water standards for the five metals tested.   SLT leachates for this material would not meet USEPA water quality criteria for lead and copper.

j.   Organic concentrations of the sediment collected for S/S treatment were low.   With or without S/S treatment, the leachate concentrations for PAHs were below the detection limit of 0.01 mg/ℓ.

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k. The addition of powdered activated carbon to the portland cement process did not significantly change the metal or organic concentrations in the TCLP leachates.

l. Heavy metal releases from S/S specimens may have been increased in the TCLP and SLT by the destruction of the physical integrity of the S/S specimens. Particle size reduction produces a greater surface area in contact with the leaching fluid, increasing the amount and rate at which substances may be leached. S/S produces a monolith that is destroyed in the particle size reduction phase of the leaching tests, possibly producing a less accurate model of leaching properties.

Recommendations

67. The information obtained from the bench-scale evaluation of S/S for Buffalo River sediment is the basis for the following recommendations:

a. Since the heavy metals in Buffalo River sediment are strongly bound to the sediment solids and are relatively resistant to leaching, S/S is not recommended as a treatment technology for the sole purpose of improving chemical stabilization of the heavy metals tested in this study. Confined disposal with appropriate design would be as effective in controlling heavy metal leachate concentrations.

b. If physical stabilization of Buffalo River sediment is an objective of a remedial action, cement is recommended as the appropriate binder on the basis of strength, durability, and leachability. An evaluation of effects of the leachate fluxes for S/S monoliths placed in a specific disposal area should be conducted before final selection of the technology.

c. Further laboratory evaluation of S/S process formulations is recommended to identify a binder or chemical agent that effectively immobilizes copper, as well as lead and other heavy metals.

40

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APPENDIX A: LABORATORY DATA

Table A1

PAH Concentrations in Buffalo River Sediment

Compound	Concentration ppm*
Acenaphthene	0.11
Acenaphthylene	<0.2
Anthracene	0.33
Benzo(a)anthracene	0.38
Benzo(b)fluoranthene + Benzo(k)fluoranthene	0.60
Benzo(G,H,I)perylene	0.16
Benzo(a)pyrene	0.33
Chrysene	0.51
Dibenzo(A,H)anthracene	<0.20
Fluoranthene	0.84
Fluorene	0.15
Indeno(1,2,3-C,D)pyrene	0.17
Naphthalene	0.29
Phenanthrene	0.73
Pyrene	0.91
Total	5.91

* Average of four analyses.

Table A2

Unconfined Compressive Strength Results
for S/S of Buffalo River Sediment

Binder Ratio	Replicate	Cure Time days	UCS psi	Average 28-Day UCS, psi
		Cement		
0.2	A	7	349	
0.2	A	14	542	
0.2	A	21	531	
0.2	A	28	479	482
	B	28	486	
	C	28	480	
0.4	A	7	994	
0.4	A	14	1,383	
0.4	A	21	1,026	
0.4	A	28	970	1,212
	B	28	1,352	
	C	28	1,314	
0.6	A	7	1,906	
0.6	A	14	1,625	
0.6	A	21	1,404	
0.6	A	28	2,071	2,063
	B	28	1,865	
	C	28	2,253	
		Kiln Dust		
0.2	A	7	72	
0.2	A	14	120	
0.2	A	21	120	
0.2	A	28	128	132
	B	28	157	
	C	28	112	
0.4	A	7	84	
0.4	A	14	139	
0.4	A	21	144	
0.4	A	28	157	177
	B	28	221	
	C	28	151	
0.6	A	7	167	
0.6	A	14	259	
0.6	A	21	210	
0.6	A	28	213	193
	B	28	134	
	C	28	231	

(Continued)

Binder Ratio	Replicate	Cure Time days	UCS psi	Average 28-Day UCS, psi
		Lime/Fly Ash		
0.2/0.2	A	7	114	
0.2/0.2	A	14	146	
0.2/0.2	A	21	135	
0.2/0.2	A	28	133	119
	B	28	105	
	C	28	118	
0.2/0.4	A	7	196	
0.2/0.4	A	14	215	
0.2/0.4	A	21	172	
0.2/0.4	A	28	240	220
	B	28	210	
	C	28	209	
0.4/0.2	A	7	152	
0.4/0.2	A	14	289	
0.4/0.2	A	21	161	
0.4/0.2	A	28	316	249
	B	28	201	
	C	28	230	
0.2/0.6	A	7	180	
0.2/0.6	A	14	333	
0.2/0.6	A	21	154	
0.2/0.6	A	28	209	218
	B	28	229	
	C	28	214	
0.4/0.4	A	7	190	
0.4/0.4	A	14	224	
0.4/0.4	A	21	298	
0.4/0.4	A	28	350	313
	B	28	300	
	C	28	287	
0.6/0.2	A	7	224	
0.6/0.2	A	14	272	
0.6/0.2	A	21	327	
0.6/0.2	A	28	319	300
	B	28	387	
	C	28	193	

(Continued)

(Sheet 2 of 4)

Table A2 (Continued)

Binder Ratio	Replicate	Cure Time days	UCS psi	Average 28-Day UCS, psi
Lime/Fly Ash (Continued)				
0.4/0.6	A	7	214	
0.4/0.6	A	14	100	
0.4/0.6	A	21	319	
0.4/0.6	A	28	278	353
	B	28	376	
	C	28	404	
0.6/0.4	A	7	90	
0.6/0.4	A	14	41	
0.6/0.4	A	21	291	
0.6/0.4	A	28	163	156
	B	28	146	
	C	28	160	
0.6/0.6	A	7	37	
0.6/0.6	A	14	124	
0.6/0.6	A	21	110	
0.6/0.6	A	28	65	110
	B	28	117	
	C	28	149	
Cement/Carbon				
0.2/0.01	A	7	355	
0.2/0.01	A	14	403	
0.2/0.01	A	21	579	
0.2/0.01	A	28	596	578
	B	28	511	
	C	28	626	
0.2/0.001	A	7	246	
0.2/0.001	A	14	493	
0.2/0.001	A	21	515	
0.2/0.001	A	28	385	495
	B	28	518	
	C	28	580	
0.2/0.0001	A	7	278	
0.2/0.0001	A	14	497	
0.2/0.0001	A	21	688	
0.2/0.0001	A	28	525	636
	B	28	655	
	C	28	729	

(Continued)

Binder Ratio	Replicate	Cure Time days	UCS psi	Average 28-Day UCS, psi
Cement/Carbon (Continued)				
0.2/0.00001	A	7	459	
0.2/0.00001	A	14	552	
0.2/0.00001	A	21	514	
0.2/0.00001	A	28	601	544
	B	28	511	
	C	28	521	

Table A3

Results of TCLP Conducted on Untreated Buffalo River Sediment

Replicate	Chromium ppm	Copper ppm	Lead ppm	Nickel ppm	Zinc ppm	pH	Conductivity μmhos/cm
A	0.004	0.026	0.063	0.079	1.02	5.5	2,000
B	0.007	0.027	0.064	0.083	0.960	5.5	2,200
C	0.003	0.028	0.064	0.084	0.954	5.5	2,000
BL	0.001	<0.010	<0.001	<0.010	0.047	4.9	420

Table A4

Results of the TCLP Conducted on S/S Buffalo River Sediment

Replicate	Chromium ppm	Copper ppm	Lead ppm	Nickel ppm	Zinc ppm	pH	Conductivity μmhos/cm
0.2 Cement							
A	0.051	0.169	<0.001	0.055	0.073	10.9	5,100
B	0.052	0.16	<0.001	0.055	0.055	11.0	6,000
C	0.054	0.163	<0.001	0.051	0.062	10.9	5,000
BL	<0.010	<0.010	<0.001	<0.010	<0.030	2.3	420
0.2 Kiln Dust							
A	0.028	0.242	<0.001	0.033	0.119	6.1	6,000
B	0.04	0.226	<0.001	0.03	0.114	6.2	6,000
C	0.044	0.212	<0.001	0.035	0.083	8.0	6,000
BL	0.022	<0.010	<0.001	<0.010	<0.030	2.9	418
0.2 Lime/0.2 Fly Ash							
A	0.034	0.139	0.113	0.033	0.141	12.3	8,500
B	0.019	0.157	0.086	0.035	0.105	12.3	9,000
C	0.016	0.179	0.11	0.034	0.104	12.3	9,000
BL	0.003	<0.010	<0.001	<0.010	<0.030	2.8	415
0.2 Cement/0.01 Carbon							
A	0.054	0.128	<0.001	0.034	0.071	10.7	6,000
B	0.054	0.116	<0.001	0.031	0.073	10.8	6,000
C	0.054	0.117	<0.001	0.034	0.07	10.8	6,000
BL	<0.010	<0.010	<0.001	<0.010	<0.030	2.8	480
0.2 Cement/0.00001 Carbon							
A	0.057	0.268	0.001	0.045	0.146	8.7	5,100
B	0.057	0.275	0.004	0.048	0.16	10.8	5,100
C	0.066	0.271	0.004	0.046	0.154	6.9	5,300
BL	<0.010	<0.010	<0.001	<0.010	<0.030	3.5	--

Table A5

Chemical Analyses of Binder Materials

Chemical Analysis	Cement Type I mg/kg	Kiln Dust mg/kg	Lime mg/kg	Fly Ash Class F mg/kg
Si	95,700	1,900	232,200	32,400
S (total)	10,800	700	1,700	31,200
Ti	1,400	50	1,000	600
P	900	60	3,200	200
Sb	<1.77	<1.63	<1.77	13.3
As	13.1	14.7	6.74	172
Be	2.13	4.24	<1.77	28.9
Cd	0.284	2.28	0.639	1.01
Cr	61.3	30.0	14.6	139
Cu	14.9	12.7	<0.355	196
Pb	2.13	15.6	<0.355	57.7
Hg	<0.100	<0.100	<0.100	<0.100
Ni	25.9	33.6	6.39	190
Se	<17.7	<16.3	<17.7	<19.5
Ag	<3.54	<3.26	<3.55	<3.90
Tl	<10.6	<9.78	<10.6	13.6
Zn	41.8	107	17.7	211
Al	23,100	13,500	238	150,000
Ba	178	119	<3.55	1,350
Ca	454,000	440,000	500,000	12,000
Cd	10.6	<9.78	10.6	77.2
Fe	25,400	14,800	1,070	50,700
Mg	5,460	3,040	2,700	6,040
Mn	503	64.2	48.6	156
Na	1,270	2,110	110	2,740
Sn	195	73.0	74.5	118
V	55.6	34.6	11.7	351

Source: Bricka, Holmes, and Cullinane 1988.

Table A6

Results of TCLP Conducted on Binders Used in S/S
of Buffalo River Sediment

Replicate	Chromium ppm	Copper ppm	Lead ppm	Nickel ppm	Zinc ppm
		Cement			
1	0.334	0.001	0.006	0.002	<0.030
2	0.307	0.001	0.002	0.002	<0.030
3	0.300	0.001	0.002	<0.001	<0.030
Average	0.314	0.001	0.004	0.0015*	<0.030
		Kiln Dust			
1	0.060	0.001	0.032	0.002	0.093
2	0.057	0.001	0.038	0.002	0.037
3	0.057	0.001	0.044	0.004	0.036
Average	0.058	0.001	0.038	0.0026	0.055
		Lime/Fly Ash			
1	0.033	0.003	0.008	0.002	0.040
2	0.024	0.008	0.006	<0.001	0.036
3	0.022	0.006	0.006	<0.001	0.100
Average	0.026	0.0056	0.0067	0.001*	0.029

Source: Bricka, Holmes, and Cullinane 1988.
 * The av rage was calculated by dividing the less-than values by 2.

Table A7

Results of SLT Conducted on Untreated Buffalo River Sediment*

Step No.	Chromium ppm	Copper ppm	Lead ppm	Nickel ppm	Zinc ppm	TOC ppm	pH	Conductivity μmhos/cm
1	0.007	0.011	0.026	<0.001	0.033	17.2	6.4	160
2	0.004	0.009	0.024	<0.001	0.042	10.7	6.4	121
3	0.003	0.006	0.016	<0.001	0.032	5.9	6.4	102
4	0.004	0.005	0.012	0.004	<0.030	5.5	6.7	97
5	0.002	0.002	0.006	<0.001	<0.030	6.1	6.7	104
6	0.001	0.003	0.003	<0.001	<0.030	--	6.7	105
7	0.003	0.004	0.004	<0.001	<0.030	--	6.3	80
Blank	<0.001	<0.001	<0.001	<0.001	<0.030	<1.0	--	--

 * Average of three replicates.

Table A8

Results of SLT Conducted on 0.2 Cement Solidified/Stabilized

Buffalo River Sediment

Step No./ Replicate	Chromium ppm	Copper ppm	Lead ppm	Nickel ppm	Zinc ppm	TOC ppm	pH	Conductivity μmhos/cm
1 A	0.008	0.220	0.017	0.110	<0.030	156	12.1	7,100
1 B							12.1	7,200
1 C							12.1	7,000
1 BL	0.029	<0.010	<0.001	<0.010	<0.030	102	9.7	25
2 A	0.030	0.143	0.014	0.065	<0.030	114	12.6	6,100
2 B							12.7	6,800
2 C							12.6	5,300
2 BL	0.015	<0.010	<0.001	<0.010	<0.030	90	10.0	30
3 A	0.013	0.090	0.016	0.040	<0.030	84	12.6	5,000
3 B	0.011	0.091	0.016	0.045	<0.030	117	12.6	6,000
3 C	0.030	0.091	0.016	0.042	<0.030	102	12.3	5,900
3 BL	0.011	<0.010	<0.001	<0.010	<0.030	60	6.0	0
4 A	0.010	0.072	0.017	0.036	<0.030	10.2	12.4	7,000
4 B							12.5	6,000
4 C							12.1	6,800
4 BL	0.001	<0.010	<0.001	<0.010	<0.030	<1.0	6.3	30
5 A	0.011	0.062	0.014	0.030	<0.030	8.3	11.9	6,800
5 B							11.4	5,700
5 C							11.3	6,100
5 BL	0.001	<0.010	<0.001	<0.010	<0.030	<1.0	4.0	20

Table A9

Results of SLT Conducted on 0.2 Kiln Dust Solidified/Stabilized

Buffalo River Sediment

Step No./ Replicate	Chromium ppm	Copper ppm	Lead ppm	Nickel ppm	Zinc ppm	TOC ppm	pH	Conductivity μmhos/cm
1 A	0.028	0.714	0.058	0.244	0.063	159	12.2	4,900
1 B							12.4	3,900
1 C							12.2	7,500
1 BL	0.002	<0.010	<0.001	<0.010	<0.030	42	5.8	0
2 A	0.024	0.357	0.056	0.089	0.065	81	12.5	6,800
2 B							12.5	6,500
2 C							12.5	5,200
2 BL	0.002	<0.010	<0.001	<0.010	<0.030	<1.0	8.8	0
3 A	0.021	0.256	0.067	0.054	0.052	20.5	12.5	6,900
3 B	0.021	0.243	0.050	0.054	0.051	20.3	12.5	8,000
3 C	0.021	0.259	0.056	0.056	0.048	88.5	12.5	7,500
3 BL	<0.010	<0.010	<0.001	<0.010	<0.030	<1.0	7.3	15
4 A	0.017	0.181	0.051	0.035	0.037	14.9	12.4	7,000
4 B							12.4	7,300
4 C							12.4	7,000
4 BL	<0.010	<0.010	<0.001	<0.010	<0.030	<1.0	9.1	0
5 A	0.016	0.172	0.043	0.035	0.045	13.5	12.4	6,500
5 B							12.5	6,000
5 C							12.5	6,500
5 BL	<0.010	<0.010	<0.001	<0.010	<0.030	<1.0	4.6	0

Table A10

Results of SLT Conducted on 0.2 Lime/0.2 Fly Ash Solidified/Stabilized

Buffalo River Sediment

Step No./ Replicate	Chromium ppm	Copper ppm	Lead ppm	Nickel ppm	Zinc ppm	TOC ppm	pH	Conductivity μmhos/c
1 A	0.018	0.435	0.049	0.111	0.047	357	12.6	7,000
1 B							12.6	7,000
1 C							12.6	7,100
1 BL	0.003	<0.010	<0.001	<0.010	<0.030	5 0	1C.3	50
2 A	0.009	0.197	0.058	0.047	0.036	<1.0	12.5	7,000
2 B							12.5	7,000
2 C							12.5	7,000
2 BL	0.001	<0.010	<0.001	<0.010	<0.030	<1.0	6.7	550
3 A	0.009	0.143	0.075	0.031	<0.030	11.3	12.0	7,000
3 B	0.009	0.144	0.054	0.024	<0.030	11.1	12.5	7,000
3 C	<0.010	0.144	0.060	0.025	0.035	11.0	12.5	7,000
3 BL	0.009	<0.010	<0.001	<0.010	<0.030	<1.0	8.1	125
4 A	<0.010	0.121	0.049	0.024	0.035	<1.0	12.0	6,500
4 B							12.0	6,500
4 C							12.0	6,000
4 BL	0.008	<0.010	<0.001	<0.010	<0.030	<1.0	9.7	10
5 A	<0.010	0.081	0.051	0.019	0.032	6.0	12.1	6,300
5 B							11.5	6,300
5 C							11.6	6,200
5 BL	0.015	<0.010	<0.001	<0.010	<0.030	<1.0	6.8	0